

NEW SECONDARY BATTERIES UTILIZING ELECTRONICALLY
CONDUCTIVE POLYMER CATHODES

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ABSTRACT

The objectives of this project are to characterize the transport properties in electronically conductive polymers and to assess the utility of these films as cathodes in lithium/polymer secondary batteries. During this research period, progress has been made in a literature survey of the historical background, methods of preparation, the physical and chemical properties, and potential technological applications of polythiophene. Progress has also been made in the characterization of polypyrrole flat films and fibrillar films. Cyclic voltammetry and potential step chronocoulometry were used to gain information on peak currents and potentials switching reaction rates, charge capacity, and charge retention. Battery charge/discharge studies were also performed.

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I. INTRODUCTION

Polythiophene is an attractive organic conducting polymer for use as a high-energy-density secondary battery because of its potential as an inexpensive, lightweight, and non-corrosive electrode material. Polythiophene has high conductivity, high specific charge density, and reversible electrochemical redox behavior to switch between conducting and nonconducting states.

The objective of this project is to develop a new secondary battery utilizing electronically conductive polythiophene. To satisfy this main objective, it is essential to understand the charge transport process and to find a morphology that optimizes the charge transport rates in electronically conductive polythiophene films.

This project is a joint project under the direction of Charles R. Martin (Department of Chemistry) and Ralph E. White (Department of Chemical Engineering). This is a joint effort because of the complementary nature of the work done by the co-principal investigators. Martin and his group provide the experimental expertise and White and his group provide data analysis and mathematical modeling expertise.

II. PROGRESS IN MARTIN'S GROUP

The purpose of this body of work is to investigate polypyrrole and lithium as electrode materials in a lightweight rechargeable battery. Lithium is a very light weight metal, and polypyrrole, also lightweight, can be doped and undoped with a counterion, making it a candidate for a rechargeable battery electrode material. We have continued to use polypyrrole rather than polythiophene because a large body of data has already been collected and, for comparison purposes, the work needed to be extended before changing to thiophene and its derivatives.

During the charge and discharge of a Li/PPy battery, the electrolyte counterion is inserted and ejected from the film (Fig. 1). This counterion insertion and ejection is the rate determining step in the switching reaction, or the changing of the polymer from a conductor to an insulator and vice versa. Counterion diffusion is much faster in solution than in the porous solid polymer. For this reason, it is advantageous to decrease the distance that the counterion has to diffuse in the polymer. Changing the morphology from a thick flat film to thin fibrils with solution channels between them decreases the counterion diffusion distance in the polymer. Also, if polypyrrole sites can be oxidized due to greater ease of counterion movement in the fibrillar film, than increased charge capacity, or total charge delivered, should result.

Experiments were designed to measure quantities that would deliver the desired information. These include cyclic voltammetry to gain information on the rechargeability and stability of the films, chronoamperometry to obtain the rate of the switching reaction and the charge capacity of the film, and battery charge/discharge curves to determine discharge voltage, time of discharge, and energy density of the battery.

A. Cyclic Voltammetry

We have continued to investigate the charge transport rates of microfibril-

lar/microporous polypyrrole synthesized in Anopore membranes. The construction of electrodes from Anopore membranes was described in our last report. Pyrrole was polymerized at a current density of 1 mA/cm^2 from a solution of 0.5M pyrrole in 0.2M Et_4NBF_4 in acetonitrile. We have modified the procedure used to extract the Anopore membranes. Previously, we treated the films with 0.2M NaOH to dissolve the Anopore. This was followed by treatment with 0.5M H_2SO_4 to remove OH^- from the film. We have now replaced the sulfuric acid solution with a 1% fluoboric acid solution. This removes any possible complication caused by the incorporation of a second counterion (i.e., sulfate as HSO_4^- or SO_4^{2-}) into the system, as BF_4^- is now the only possible counterion in the system. The films were electrochemically characterized in a solution of 0.2M Et_4NBF_4 in acetonitrile using cyclic voltammetry and potential step chronocoulometry. These results will be discussed below.

1. Effects of Base/Acid Extraction Procedure on Conventional Polypyrrole Films

Figure 2 shows the cyclic voltammetry of a $0.5 \mu\text{m}$ conventional polypyrrole film before and after treating it with the procedure used to extract Anopore membranes. The base/acid treatment causes the anodic (oxidation) wave to be broadened. The peak is negatively shifted by ca. 50 mV. While the peak current is smaller for the treated film than for the untreated film, the total charge under the curve remains the same. The fact that the total charge remains the same indicates that the number of electroactive sites is the same before and after treatment. The extraction procedure has very little effect on the cathodic (reduction) wave for thin films. For thicker films ($\pm 1.0 \mu\text{m}$) the cathodic wave is also broadened.

2. Microfibrillar Polypyrrole

Figure 3 shows the cyclic voltammetry of a conventional $1.0 \mu\text{m}$ thick polypyrrole

film (untreated) and the equivalent amount of polymer in fibrillar form (after extraction of Anopore). Figure 4 shows the cyclic voltammetry of a $1.0\ \mu\text{m}$ conventional polypyrrole and fibrillar film which have both been treated with the extraction procedure. The anodic (oxidation) wave is broader than that of conventional polypyrrole. It is negatively shifted by ca. 100 mV compared to untreated conventional polypyrrole and is ca. 50 mV negative of treated conventional polypyrrole. The cathodic (reduction) wave is also negatively ca. 50 mV. However, the most interesting feature of the fibrillar polypyrrole is the narrow cathodic (reduction) wave. This suggests that the reduction reaction is much faster for fibrillar than conventional polypyrrole films. This is important since the reduction of polypyrrole occurs during battery discharge when polypyrrole is used as a battery cathode. The faster this reaction is the higher the current density which can be drawn from the battery will be.

B. Potential Step Chronocoulometry

1. Comparison of Fibrillar Films to Treated Flat Films

Our previous report compared the chronocoulometry of fibrillar polypyrrole to untreated polypyrrole films. We now compare the chronocoulometry of fibrillar polypyrrole to conventional polypyrrole films which have been treated identically. The earlier studies used an initial potential of $-0.6\ \text{V}$ and final potential of $+0.2\ \text{V}$ vs. the SCE for the oxidation step and vice versa for the reduction step. We have now shifted these to $-0.65\ \text{V}$ and $+0.15\ \text{V}$ based on the $-50\ \text{mV}$ shift of the peaks observed in the cyclic voltammetry of polypyrrole treated with the base/acid extraction procedure. Table 1 shows the chronocoulometric data for fibrillar and conventional polypyrrole films (treated and untreated). The most notable and important feature of this table is the significantly faster rate of reduction of fibrillar polypyrrole.

2. Comparison of Charge Retention

The following potential step studies were carried out in 0.2M ET_4NBF_4 in acetonitrile. Experiments were conducted in a glove bag and all solutions were degassed with N_2 for a minimum of 15 minutes before use. Films were grown at a constant current of 1 mA/cm^2 until 67 mC of charge had been passed. This number, 67 mC, is the number of coulombs needed to grow a 1 micron film on a 0.178 cm^2 platinum disk according to the Penner ratio of charge vs. film thickness. The same amount of charge was used in making the fibrillar polypyrrole electrodes so that the two types of electrodes would contain the same amount of polymer and could be compared to one another. The electroactive surface area of the fibrillar electrode was calculated to be 0.5702 cm^2 by multiplying the geometric surface area, 0.9503 cm^2 by 60%, which is the porosity of Anopore membranes used to make the electrodes.

The fibrillar version of the polypyrrole electrodes must be subjected to 0.2M NaOH to dissolve the host Anopore membrane and 1N H_2SO_4 to remove OH^- from the polymer. Therefore, for purpose of comparison, the flat PPy films were also treated in a similar manner.

Potential was stepped from the foot of the oxidation wave to the foot of the reduction wave, and vice versa. Current/time transients were recorded, and the data were integrated to obtain charge/time transients. Cyclic voltammetry showed that the oxidation and reduction waves were both shifted 50-100 mV to the negative after treatment with acid and base. Therefore, the potentials at which the steps were performed on the treated and fibrillar films were shifted 100 mV to the negative, i.e., potentials of the films were stepped from +0.1 V to -0.7 V and back again instead of from +0.2 V to -0.6 V and back again. A study of the charge capacities of 1st vs. 2nd oxidations and reductions of both fibrous and flat films indicate that the flat film

could be less able to expel counterions than the fibrillar film. If the flat film is unable to eject all the counterions after the first oxidation, its charge capacity would be lower in subsequent steps.

While the subsequent oxidations and reductions of flat films consistently show a decreased charge capacity (Figs. 5,6), the subsequent oxidations and reductions of the fibrillar film show near constant or even increased charge capacity (Figs. 7,8).

These studies show that retention of charge capacity is better in fibrillar films than in flat films upon multiple reductions and oxidations of the film. A better battery cycle life should result from a battery made with a fibrillar polypyrrole electrode.

C. Battery Studies

In order to compare these studies with other work in the literature (1), a 1M solution of LiClO_4 in propylene carbonate was used. A Li counterelectrode and a polypyrrole working electrode were employed, and the reference electrode was Ag/Ag^+ (0.2M AgNO_3). All potentials are reported as Ag/Ag^+ . A 1.5μ film was grown at $1 \text{ mA}/\text{cm}^2$ and $+0.4 \text{ V}$. After reducing the film at -1.2V , a cyclic voltammogram was taken (Fig. 9). Compared to previous work reported in the literature (Fig. 10), the peaks in Fig. are more distinct and narrower. Also in Fig. 9, there is a greater capacitive current, indicating conductivity, in the most positive potential region where the polymer is oxidized. No such region is evident in Fig. 10. Likewise, in the most negative potential region where the polymer should be reduced, there is an absence of current in Fig. 9, indicating that the polymer is an insulator in this potential region. There is no such indication in Fig. 10. Therefore, the films grown in our lab should be able to be charged and discharged more completely than those films shown in the literature. After the cyclic voltammogram was recorded, the film was again reduced completely before charging. It was then charged at $1 \text{ mA}/\text{cm}^2$ for a time, then

discharged at the opposite current density for the same time period. Results are shown in Fig. 11. The equation for experimental energy density is

$$e.d. = \frac{iVt'A}{m}$$

where i =current density, V =cell discharge voltage, t' =the time at which the battery can no longer sustain a contact potential during discharge, m =mass, and A =electrode area. In this example, $i=1$ mA/cm², $V=1$ V, $t'=125$ sec, $A=0.32$ cm², and $m=83.2$ μ g. Therefore, $e.d.=134$ Wh/kg for this battery.

D. Conclusion

These studies conclusively show that the reduction rate of fibrillar polypyrrole is significantly faster than that of conventional polypyrrole. This implies that one could expect significantly higher current densities from polypyrrole batteries if fibrillar polypyrrole is used in place of conventional polypyrrole. Future work will concentrate on demonstrating this.

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III. PROGRESS IN WHITE'S GROUP

Polythiophene and its derivatives can be chemically or electrochemically synthesized. By chemical or electrochemical doping (oxidation) or undoping (reduction), the electronic conductivity of polythiophene can be varied over 12 orders of magnitude, with properties ranging from insulator ($10^{-10} \Omega^{-1}\text{cm}^{-1}$) to conductor ($10^2 \Omega^{-1}\text{cm}^{-1}$). This report reviews the historical background (2-13), the synthesis and structure (14-36), the chemical and physical properties (37-41), and the potential technological applications (41-59) of polythiophene. This review shows that polythiophene and its derivatives are the first class of candidates for practical applications because of their high conductivity, reversibility, and stability.

A. Historical Background

A new chapter in the evolution of organic conducting polymers began with the discovery of polyacetylene, $(\text{CH})_x$, in 1977 (2, 3, 4). The discovery of this semiconducting and metallic organic polyacetylene introduced new concepts in the field of the organic conducting polymers and intensified research in the synthesis and characterization of this class of compounds.

Polyacetylene is one of the simplest linear conjugated polymers with a single-chain structure. It was found that exposure of films of either *cis*- or *trans*- $(\text{CH})_x$ to iodine, bromine, or arsenic pentafluoride vapour led to an oxidized form (p-type) while treatment with a solution of sodium naphthalide led to a reduced form (n-type). In 1979, it was discovered that p- or n-type $(\text{CH})_x$ could be accomplished electrochemically and that these processes were electrochemically reversible (5). Moreover, the oxidation or reduction of the film was accompanied by an increase in conductivity from $10^{-8} \Omega^{-1}\text{cm}^{-1}$ for the natural film to a value of up to $10^3 \Omega^{-1}\text{cm}^{-1}$ for the oxidized film. These led naturally to the conclusion that $(\text{CH})_x$ and its various oxidized or reduced

forms might act as promising charge storing materials for use in secondary batteries. Polyacetylene had been extensively investigated as an electrode material in secondary battery technologies (6, 7). However, the main problem with using polyacetylene as an electrode material is its poor stability in the presence of oxygen and water (8).

The discovery of polyacetylene touched off a flurry of research directed towards the study and discovery of new conducting polymeric systems such as polypyrrole (9, 10), polyparaphenylene (11), and polythiophene (12, 13). The potential applications for most of these new polymers in the field of conductors, organic batteries, and display devices depend on their reactivity with oxygen and moisture. In this respect, discovery of polythiophene and its derivatives are particularly significant since they are extremely stable in both oxygenated and humid environments, even in their neutral (reduced) state.

B. Polymerization

Polythiophene and its derivatives can be synthesized by either chemical or electrochemical procedures. A chemical route generally leads to its undoped insulating state; it can be doped chemically or electrochemically to its conducting state. In contrast, an electrochemical route yields directly in its oxidized conducting state; its thickness can be well controlled by the electrolysis time. It can subsequently be reduced chemically (NH_3) or electrochemically to its insulating state.

1. Chemical Polymerization

Thiophene has been polymerized with a variety of initiators: sulfuric acid (14), iron(III) chloride (15), and Ziegler catalysts (16). However, experimental data show that with an acidic promoter, polythiophene consists of alternating thiophene and tetrahydrothiophene units (17, 18).

Yamamoto *et al.* (12) have synthesized polythiophene on the catalytic coupling of the Grignard reagent of 2,5-dibromothiophene or 2,5-dihalogenothiophene by nickel salt. The general procedure consists of stirring 2,5-dibromo- (or 2,5-dihalogeno-) thiophene with freshly distilled tetrahydrofuran (THF) and magnesium. The catalyst, nickel acetylacetonate, nickel chloride, or copper chloride, is dissolved in THF and introduced. After 4 hours the mixture is cooled and poured into methanol-HCl. The obtained solid is then washed in methanol and dried.

Polythiophene also can be synthesized by bringing together the monomer or the dimer and the complex AsF_5 (19-20). The resulting polymers are generally black and insoluble; their compositions depend on the AsF_5 pressure and the reaction time.

2. Electrochemical Polymerization

Several results have been published on the electrochemical synthesis of polythiophene and its derivatives (13,21-25). The most widely used electrochemical technique is to use single-compartment electrochemical cell with three electrode configuration:

- (a) working electrode; Pt, Au, or glass coated with SnO_2 or In_2O_3 ,
- (b) reference electrode; saturated calomel electrode (SCE),
- (c) and auxiliary electrode; Pt, Ni, or C electrode.

The electrolytic medium typically consists of an organic solvent (e.g., acetonitrile, THF, dichloromethane, or benzonitrile), a supporting electrolyte MX ($\text{M}^+ = \text{N}(\text{Bu})_4^+$, Li^+ ; $\text{X}^- = \text{ClO}_4^-$, BF_4^- , PF_6^- , SO_3CF_3^-), and a thiophene monomer (0.1M to 1M). The solvent, the monomer, and the supporting salt are generally purified by distillation or recrystallization just prior to electrolysis. The water content of the electrolytic medium lies in the range 0.01M and the solutions are degassed prior to electrolysis by argon bubbling.

The polythiophene films can be grafted on the electrode with either a controlled

potential or a controlled current. Electrochemical polymerization of thiophene yields an oxidized conducting form because the aromatic dimer and higher molecular weight oligomers have lower oxidation potentials than the monomer; for example, the oxidation potential is +1.65 V (vs. SCE) for thiophene and +1.1 V (vs. SCE) for the corresponding polymer. The film thickness is well controlled by the electrolysis time; films between some angstroms to several millimeters have been deposited with a linear charge thickness relationship of 10 \AA/mC-cm^2 . The structure and the electrical properties of the polymers do not depend on the electrochemical conditions unless too fast a growth rate (several thousands of angstroms per minute) is used, which leads to less homogeneous and less regular films.

C. Structure and Polymerization Mechanisms

1. Structure

Figure 12 shows the general structure of polythiophene which corresponds to the coupling of monomeric units in 2,5-positions with preservation of the aromatic nucleus (12,21,26). The dominance of the α,α' -linkage in polythiophene and its derivatives has been confirmed by ^{13}C nuclear magnetic resonance spectrum analysis (27-28). However, analysis shows that the polymer is far from ideal, with less than two-thirds of the repeat units in this form (29). There is some involvement of the β -carbons in the chain bonding which could cause some crosslinking of the polymer (29). Chemical analysis suggests that the fully oxidized PPy film consists of approximately three pyrrole rings per perchlorate anion (29). There are no reports of doping with cations by the reduction of the neutral film.

Some differences are observed between chemical and electrochemical synthesis. With electrochemical synthesis, impurities due to supporting salt or secondary elec-

trochemical reactions have never been detected. In contrast, structural defects and/or impurities are generally observed with the chemical path. For example, Mg and/or Ni present in the catalysis reaction (12), and As_4O_6 and As_3O_4 present in the polymer with the AsF_5 synthesis (19-20).

2. Polymerization Mechanisms

The mechanism of the electrochemical polymerization has been discussed by several authors (29-32). However, a detailed mechanism has yet to be unambiguously established. The generally accepted mechanism of the electrochemical polymerization of the polythiophene is radical coupling mechanisms as shown in Fig. 13 (32).

The polymerization mechanism is believed to proceed via the radical cation monomer. The radical cation species resulting from the oxidation of thiophene monomer is unstable and highly reactive. Therefore, it reacts immediately with a second radical cation of the monomer to give a dimer by the elimination of two protons (33-35). At the potential needed to oxidize the monomer, the dimer or higher oligomers would also be oxidized and these could react further with the radical cation of the monomer to build up the polymer chain. A second contributing factor may be migration of anion, which occurs to a greater extent at more positive potentials to augment the anion concentration near the electrode (36). The chain growth is terminated either when the radical cation of the growing chain becomes un-reactive or, more likely, when the reactive end of the chain becomes sterically blocked (33). The final polymer chain bears a charge of unity for every two to four thiophene rings, this charge being counterbalanced by the anion of the electrolyte salt.

Cyclic voltammetry and step potential experiments (31) show that the formation of monomers on the surface of the electrode is via a nucleation and growth mechanism. The role and positioning of the anion in the film remains one of the key questions in

the electrochemical polymerization of polythiophene.

D. Properties

1. General Properties (37-38)

Polythiophene and its derivatives are insoluble and infusible. Thus the determination of their molecular weight is quite difficult.

Polythiophene and its derivatives are stable up to 350°C in air and up to 900°C in inert gas or under vacuum.

Polythiophene and its derivatives are attacked in concentrated acidic medium but are attacked more slowly in concentrated basic solutions.

The densities of these polymers, determined by the flotation technique, lie in the range 1.4-1.6 g/cm³.

2. Morphology

The morphology of the polythiophene and its derivatives mainly depends on three parameters: the structure of the monomer, the nature of the dopant, and the thickness of the film. When polythiophene and its derivatives are grafted as thin films (less than 2000 Å), scanning electron microscopy (SEM) analysis shows that the surface is very homogeneous, whatever the polymer and the anion used. However, when the film thickness is increased to about 0.5-1 μm, the surface is no longer homogeneous and defects appear, depending now on the polymer and on the anion.

When the polymer thickness is increased to a few microns, a powdery deposit rather than a smooth film is obtained. Structural defects, such as crosslinking, reticulation, or β- instead of α-coupling for thiophene units, can account for the decrease in polymer regularity.

3. Electrochemical Properties

The polythiophene films are electroactive and can be switched between the natural nonconducting (undoping) state and the oxidized conducting (doping) state with a change of doping level. The change in doping level is accompanied by strong changes in both conductivity and spectral properties. The redox reaction is chemically reversible and can be driven repeatedly without loss of electroactivity. Electrochemical switching between conducting and insulating states can be well presented by a cyclic voltammetric techniques as shown in Fig. 14 (39).

Figure 14 shows cyclic voltammograms of a 250 nm thick film of poly-3-methylthiophene at various sweep rates of 20, 50, and 100 mV/sec. Electrolytic medium contains 0.1M LiClO₄, 0.01M H₂O and CH₃CN. Each cyclic voltammogram involves an equal amount of charge in both oxidation and reduction processes. The oxidation wave is symmetric and well defined, while the reduction wave is very wide and contains two peaks, which must be associated with a rearrangement mechanism in the polymer.

The oxidation or doping of the polymer corresponds to the transfer of an electron from the polymer to the electrode, producing a hole, and then to the migration of this hole by a hopping mechanism to the film electrolytic medium. An anion-hole pair can then diffuse back into the polymer, maintaining electron neutrality. This phenomenon repeats itself until all electroactive sites are oxidized. The symmetrical and well defined oxidation peak suggests that diffusion phenomena do not control the rate of oxidation.

The reduction or undoping of the polymer is more complex and extends over a large potential range. The reduction wave is significantly broader than the oxidation wave. The broadening of the observed reduction peak is currently not well understood, but these effects could be explained on the basis of a large uncompensated resistance caused by the reduced polymer film (40). In the reduced, or neutral state, polythiophene has

a high ionic resistance because of the presence of an ion gate.

Both anodic and cathodic voltammograms are broader than expected for a Nernstian redox couple. The large background capacitive currents once oxidation is completed can be explained by the fact that polythiophene is effectively a metal electrode with a high surface-to-volume ratio which is porous to solvent and electrolyte ions, and this porosity is responsible for the apparent reversible electrochemical behaviour.

A distinctive color change accompanies the redox reaction involving polythiophene (41). The colors observed reflect the solid state electronic properties of the polymer in each of its redox states. Oxidized conducting polythiophene is deep blue due to the existence of interband electronic transitions. In contrast, reduced, nonconducting polythiophene is red to the existence of a substantial band-gap. In the neutral state, red polythiophene has a strong absorption band in the ultraviolet-blue range and the absorption in the visible range increases when the film is oxidized, giving the coating a blue color (41). The red color of polythiophene during electrochemical cycling of the polymer between reduced and oxidized redox states indicates that the polymer is quantitatively reduced.

4. Chemical and Electrochemical Stability

A key problem of the organic conducting polymers in practical applications is their poor stability in the presence of air and moisture. Thus, it was very important to address this problem with polythiophene. Comparative results have been published on polythiophene (38).

Doped and undoped polythiophene and derivatives have been characterized by IR, ESR, elemental microanalysis, and DC conductivity just after their synthesis and after eight months storage in air. The storage in air of doped polymers affects neither

the doping level nor the conductivity. The undoped polythiophene behaves in the same way. After eight months of storage in ambient air, neither oxygen nor H_2O could be detected. Furthermore, polythiophene can be doped after eight months to the same level as before, about 25-30%. Polythiophene should be stable to oxygen and water because its redox potential lies far from the O_2 reduction potential and the H_2O oxidation potential (38).

Polythiophene and its derivatives also have excellent stability under electrochemical treatment. The polymers can be cycled between their doped and undoped states without significant degradation.

E. Applications

The great chemical and electrochemical stability in air and in moisture together with the possibility of doping in aqueous medium make polythiophene and its derivatives good candidates for practical applications (41-59).

1. Display Devices

Serious attention has been focused on the application of polythiophene as the active element in display devices (41). Polythiophene and its derivatives are electrochemically grafted as thin layers on a Pt, Au, or SnO_2 electrode and can be reversibly cycled between their oxidized and neutral states, characterized by different optical absorption spectra (red to deep blue). This feature makes electronically conductive polythiophene as an attractive candidate for electrochromic display.

A color change occurs as a result of the absorbance induced by the passage of a charge between the conducting and insulating states (42-43). The mechanism assumes the ion insertion by electrochemical reactions where the color change is a result of the insertion of ions from an electrolyte and electrons from an electrode.

The main limitations lie either in a long switching time or in a poor operating life. Thus many parameters such as the purity of the electrolytic medium, the maturity of the solvent and of the electrolyte, and the structure and homogeneity of the film must be controlled to improve the electrochromic properties of these devices (41).

2. Energy Storage

The reversible doping-undoping process of polythiophene films makes them good candidates for secondary battery electrodes. Several configurations have been studied. The first one has a Zn negative electrode, a ZnI_2 electrolyte, and a I_2 doped polythiophene positive electrode (44). The other configuration uses an organic medium which allows high performances; polythiophene/propylene carbonate- LiClO_4/Li or polythiophene/acetonitrile- $\text{N}(\text{Bu})_4\text{BF}_4/\text{polythiophene}$ (45-48). The polymer is electrochemically grafted as thin films or thick deposits on Pt, Au, or ITO, undoped, and immersed in the electrolytic medium.

The polythiophene secondary batteries have a high open circuit of 3.1-3.9 V, an energy density of 75-240 Wh/kg (same range as lead acid battery), but a power density of more than 40,000 W/kg (compared to 850 W/kg for the lead acid battery). This high power density must be related to the porous nature of polythiophene resulting in high current densities and to the large diffusion coefficient values obtained for the anion. However, two main problems limit the development of secondary organic batteries: the stability of the organic solvent against a high open circuit voltage and the autodischarge of the polymer in the electrolytic medium.

3. Solar Energy Conversion

Two configurations have been studied using polythiophene derivatives in photovoltaic applications: the conversion of solar energy in electricity with the undoped

semiconducting polymers as the photoactive material, and protection against photo-corrosion or photopassivation of small band gap semiconductors (Si, GaAs) in photoelectrochemical cells by grafting thin conducting polythiophene films on the surface.

First, thin films of undoped polythiophene and derivatives grafted on Pt or Au are used in the construction of photovoltaic cells (49): dry cell (Pt/polythiophene/Al) and electrolytic cell (Pt/polythiophene/electrolytic medium).

Second, polythiophene films can serve as a pacifying layer for the basic component in solar energy cells and photoelectric devices. The development of photoelectrochemical cells is mainly limited by the problem of photodegradation of small band gap semiconductors (50). The polythiophene films can be grown on n-type semiconductors (such as, Si, GaAs, CdS, CdSe, and CdTe) in the photoelectrochemical cells by photo assisted electrochemical oxidation of the monomer. A thin layer of polythiophene deposited on n-type photoanodes effectively inhibits the dissolution or oxidation of the n-type semiconductor, thus extending lifetime of photoelectrochemical cells (51-58).

A problem encountered with this application is that the film does not adhere to the electrode surface over a long period of time. Efforts are being made to solve this problem. For example, Fan *et al.* (55) and Skotheim *et al.* (56) reported an improvement in film adhesion by metallizing the Si surface prior to polymerization of the polymer monomer. Other methods of improving the film adhesion include chemical binding of the film to the electrode (53,58).

4. Catalysis

A lot of work has been devoted to the physicochemical properties of metallic clusters or aggregates, owing to their interesting applications in the field of catalysis (59). The major problem encountered concerns the migration and aggregation of the highly dispersed phase which lowers the catalytic activity. One approach to decrease

this aggregation process involves the use of organic conducting polymers which combines the two features of the catalytic and electroactive sites.

The high stability of polythiophene derivatives and the possibility of doping in water make them good candidates for the assembly of catalytic systems. Recently the electrochemical conditions allowing the inclusions of Ag, Cu, and Pt aggregates in PMeT together with the analysis of their catalytic properties toward the H^+ reduction into H_2 have been published (59).

F. Conclusion

Polythiophene and its derivatives can be chemically or electrochemically synthesized and subsequently can be reversibly doped and undoped.

Structural defects and impurities are generally detected when the polymer is synthesized chemically, which decreases the doping level and the conductivity. In contrast, with electrochemical synthesis, high doping levels (up to 50%) and high electronic conductivity (up to $100 \Omega^{-1}cm^{-1}$) have been achieved by varying the structure of the polymer and the nature of the dopant.

An important feature of these polymers is their good chemical and electrochemical stability in air and moisture in both the doped and undoped states, in contrast to most other organic conducting polymers.

This remarkable property together with the possibility of doping in aqueous media make them good candidates for practical applications, for example, in the fields of energy storage, solar energy conversion, and catalysis.

IV. FUTURE STUDY

A. Martin's Group

In the immediate future, studies will include the construction of a battery with a fibrillar polypyrrole electrode which will be compared to the battery with a flat polypyrrole film electrode. Cyclic voltammetry, chronoamperometry, and charge/discharge curves will be performed on both fibrillar and flat film batteries and results will be compared. Similar studies will then be carried out using poly-3-methylthiophene or a derivative thereof.

B. White's Group

A basic literature survey has been done of the fundamental aspects of the polythiophene film. Future work in this area will characterize uncertain electrochemical properties and charge transport phenomena based on the known information for future application. We are planning to study of the electrode mechanisms and transport phenomena which affect the performance of the polythiophene electrode process.

REFERENCES

1. T. Osaka, K. Naoi, S. Ogano, and S. Nakamura, *J. Electrochem. Soc.*, **134**, 2096 (1987).
2. H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 578 (1977).
3. C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. MacDiarmid, *Phys. Rev. Lett.*, **39**, 1098 (1977).
4. C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, and H. Shirakawa, *J. Am. Chem. Soc.*, **100**, 1013 (1978).
5. P. J. Nigrey, A. G. MacDiarmid, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 594 (1979).
6. P. J. Nigrey, D. MacInnes, Jr., D. P. Nairns, A. G. MacDiarmid, and A. J. Heeger, *J. Electrochem. Soc.*, **128**, 1651 (1981).
7. P. J. Nigrey, A. G. MacDiarmid, and A. J. Heeger, *Mol. Cryst. Liq. Cryst.*, **83**, 309 (1982).
8. J. R. Ellis, "Handbook of Conducting Polymers, Volume 1", T. A. Skotheim, Ed., p. 489, Marcel Dekker, Inc., New York (1986).
9. A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, 635 (1979).
10. K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt, and G. B. Street, *J. Chem. Soc., Chem. Commun.*, 854 (1979).
11. L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, *Synth. Met.*, **1**, 307 (1979/1980).
12. T. Yamamoto, K. Saneckika, and A. Yamamoto, *J. Polym. Sci. Polym. Lett. Ed.*, **18**, 9 (1980).
13. K. K. Kanazawa, A. F. Diaz, M. T. Krounbi, and G. B. Street, *Synth. Met.*, **4**, 119 (1981).
14. V. Meyer, *Chem. Ber.*, **16**, 1465 (1883).
15. J. Bruce, F. Challenger, H. B. Gibson, and W. E. Allenby, *J. Inst. Pet.*, **34**, 226 (1948).
16. A. V. Topchiev, Y. Y. Gol'dfact, and B. A. Krentsel, *Vysokomol. Soedin.*, **3**, 870 (1961).
17. P. Kovacic and K. N. McFarland, *J. Polym. Sci. Polym. Chem. Ed*, **17**, 1963 (1979).
18. S. L. Mersel, G. C. Johnson, and H. D. Hartough, *J. Am. Chem. Soc.*, **72**, 1910 (1950).
19. G. Kossmehl and G. Chatzitheodorou, *Makromol. Chem. Rap. Commun.*, **2**, 551 (1981).
20. G. Kossmehl and G. Chatzitheodorou, *Mol. Cryst. Liq. Cryst.*, **83**, 291 (1982).
21. G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, **135**, 173 (1982).
22. K. Kaneto, K. Yoshino, and Y. Inuishi, *Jpn. J. Appl. Phys.*, **21**:L, 567 (1982).
23. S. Hotta, T. Hosaka, and W. Shimotsuna, *Synth. Met.*, **6**, 317 (1983).

24. M. S. Druy and R. J. Seymour, *J. Phys. Paris Colloq.* **C3**, 44, 595 (1983).
25. G. Zotti and G. Schiavon, *J. Electroanal. Chem.*, **163**, 385 (1984).
26. C. Z. Hotz, P. Kovacic, and I. A. Khoury, *J. Polym. Sci. Polym. Chem. Ed*, **21**, 2617 (1983).
27. S. Hotta, T. Hosaka, and W. Shimotsuma, *J. Chem. Phys.*, **89**, 954 (1984).
28. S. Hotta, T. Hosaka, M. Soga, and W. Shimotsuma, *Synth. Met.*, **9**, 87 (1984).
29. G. B. Street, T. C. Clarke, M. Krounbi, K. K. Kanazawa, V. Lee, P. Pfluger, J. C. Scott, and G. Weiser, *Mol. Cryst. Liq. Cryst.*, **83**, 253 (1982).
30. R. J. Waltman and J. Bargon, *Can. J. Chem.*, **64**, 76 (1986).
31. S. Asavapiriyant, G. K. Chandler, G. A. Gunawardena, and D. Pletcher, *J. Electroanal. Chem.*, **177**, 229 (1984).
32. E. M. Genies, G. Bidan, and A. F. Diaz, *J. Electroanal. Chem.*, **149**, 101 (1983).
33. G. B. Street, T. C. Clarke, R. H. Geiss, V. Y. Lee, A. Nazzal, P. Pfluger, J. C. Scott, *J. Phys. Paris Colloq.*, **599**, C3 (1983).
34. G. B. Street, R. H. Geiss, S. E. Lindsey, A. Nazzal, and P. Pfluger, "Proceedings of the conference on electronic Excitation and Interaction Process in Organic Molecular Aggregates", P. Reineker, H. Hakn, and H. C. Wolf, Ed., p. 265, Springer, New York (1983).
35. A. F. Diaz, V. Vasquez, and A. M. Duran, *IBM J. Res. Dev.*, **25**, 42 (1981).
36. R. J. Waltman, A. F. Diaz, and J. Bargon, *J. Phys. Chem.*, **88**, 4343 (1984).
37. T. Yamamoto, K. Sanachika, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **56**, 1497 (1983).
38. G. Tourillon and F. Garnier, *J. Electrochem. Soc.*, **130**, 2043 (1983).
39. G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, **161**, 51 (1984).
40. P. Burgmayer and R. W. Murray, "Handbook of Conducting Polymers, Volume 1", T. J. Skotheim, Ed., p. 507, Marcel Dekker, New York (1986).
41. M. Gazard, "Handbook of Conducting Polymers, Volume 1", T. J. Skotheim, Ed., p. 673, Marcel Dekker, New York (1986).
42. A. F. Diaz and K. K. Kanazawa, *Chem. Scr.*, **17**, 145 (1981).
43. A. F. Diaz, M. Salmon, and J. Addy, *Proceedings of the First European Display Research Conference*, Munich, p. 111, VDE-Verlag GmbH, Berlin (1981).
44. T. Yamamoto, in Spring Electrochemical Society Meeting Extend Abstracts, Vol. 82-1, Electrochemical Society, 1982, p. 987.
45. A. R. Kmetz and F. K. Von Willisen, *Non-Emissive Electrooptic Displays*, Plenum, New York (1976).
46. K. Kaneto, K. Yoshino, and Y. Inuishi, *Jpn. J. Appl. Phys.*, **22**:L, 567 (1983).
47. J. C. Dubois, G. Tourillon, and F. Garnier, French Patent No. 8209513 (1982).
48. R. J. Waltman, A. F. Diaz, and J. Bargon, *J. Electrochem. Soc.*, **131**, 740 (1984).
49. S. Glenis, G. Horowitz, G. Tourillon, and F. Garnier, *Thin Solid Films*, **111**, 93 (1984).
50. G. Horowitz, G. Tourillon, and F. Garnier, *J. Electrochem. Soc.*, **131**, 151 (1984).
51. R. Noufi, A. J. Frank, and A. J. Nozik, *J. Am. Chem. Soc.*, **103**, 1849 (1981).

52. R. Noufi, D. Tench, and L. F. Warren, *J. Electrochem. Soc.*, **127**, 2310 (1980).
53. A. J. Frank, *Mol. Cryst. Liq. Cryst.*, **83**, 341 (1982).
54. R. Noufi, D. Trench, and L. F. Warren, *J. Electrochem. Soc.*, **127**, 1625 (1980).
55. F. F. Fan, B. Wheeler, A. J. Bard, and R. Noufi, *J. Electrochem. Soc.*, **128**, 2042 (1981).
56. T. Skotheim, O. Inganäs, J. Prejza, and I. Lundström, *Mol. Cryst. Liq. Cryst.*, **83**, 329 (1982).
57. T. Skotheim, I. Lundström, and J. Prejza, *J. Electrochem. Soc.*, **128**, 1625 (1981).
58. A. J. Frank and R. J. Honda, *J. Phys. Chem.*, **86**, 1933 (1982).
59. G. Tourillon and F. Garnier, *J. Phys. Chem.*, **88**, 5281 (1984).

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Table 1. Summary of chronocoulometric studies.

Fibrillar Polypyrrole

Amount of Polypyrrole μmoles	Approximate Thickness (μm)	Switching Time (seconds)		Total Charge Delivered (nC)	
		oxidation	reduction	oxidation	reduction
0.44	0.5	2.2	2.05	10.7	10.2
0.88	1.0	2.95	2.05	20.7	20.4
1.31	1.5	5.5	4.25	28.2	27.6
1.75	2.0	5.8	5.95	39.7	36.4

Untreated Conventional Polypyrrole

Amount of Polypyrrole μmoles	Approximate Thickness (μm)	Switching Time (seconds)		Total Charge Delivered (nC)	
		oxidation	reduction	oxidation	reduction
0.44	0.5	2.2	3.1	10.6	8.8
0.88	1.0	3.5	6.0	20.4	18.6
1.31	1.5	4.9	6.5	31.2	28.0
1.75	2.0	6.4	10.2	38.4	39.2

Treated Conventional Polypyrrole

Amount of Polypyrrole μmoles	Approximate Thickness (μm)	Switching Time (seconds)		Total Charge Delivered (nC)	
		oxidation	reduction	oxidation	reduction
0.44	0.5	1.65	1.45	10.0	9.8
0.88	1.0	4.3	4.3	18.5	17.3
1.31	1.5	4.95	9.6	29.0	26.6
1.75	2.0	8.1	14.7	39.1	34.2

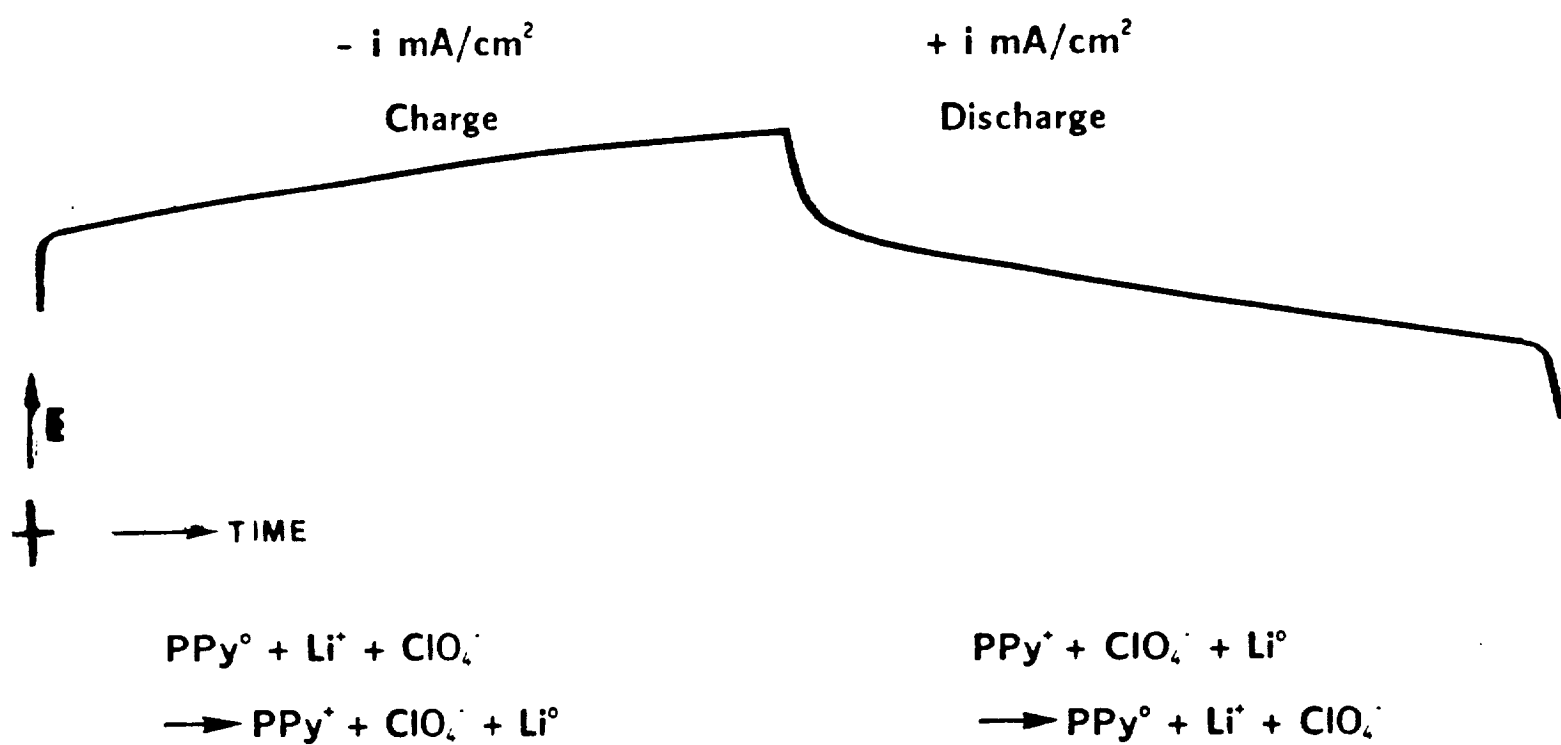


Fig. 1. Charge/Discharge curve of Li/1M LiClO₄/PPy Battery.

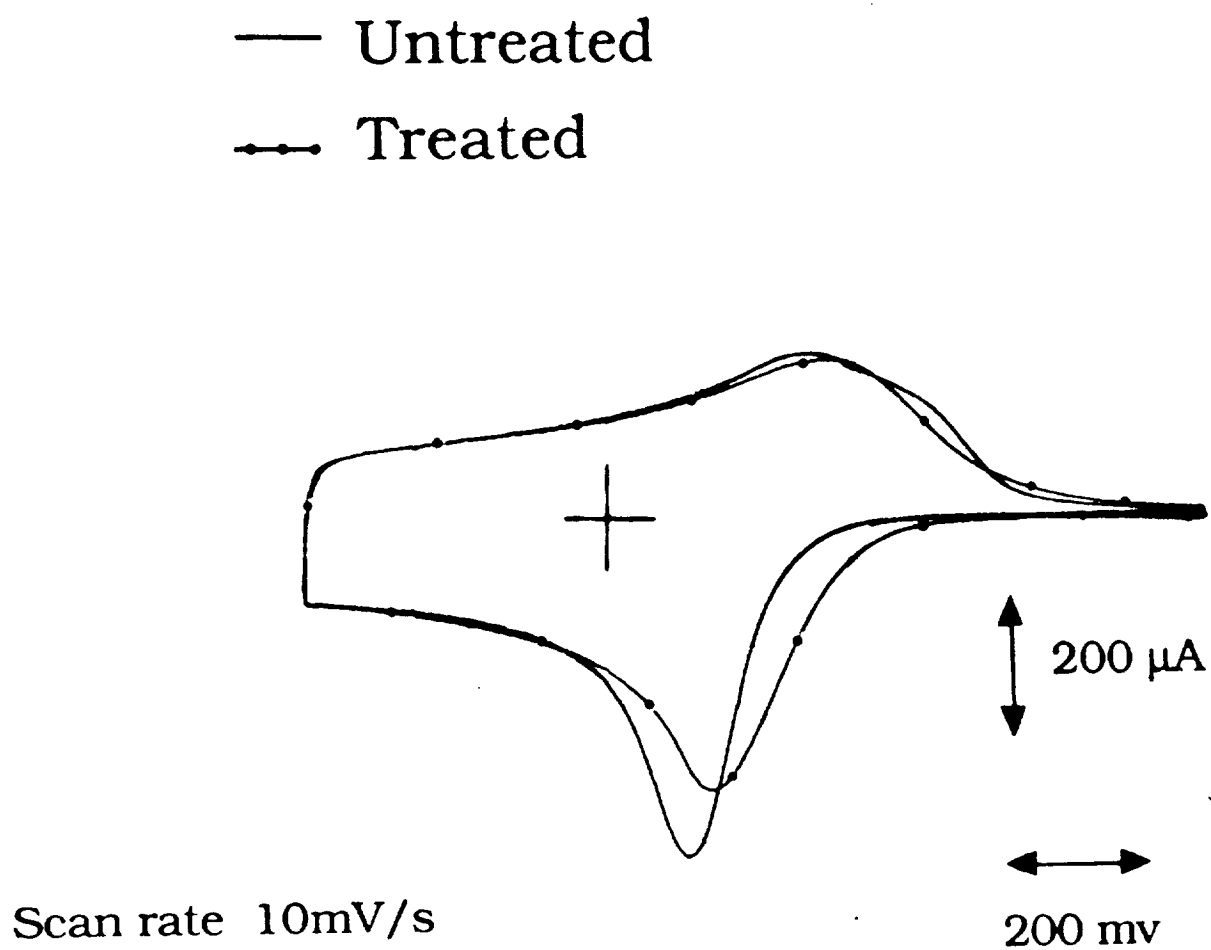


Fig. 2. Cyclic voltammograms of 0.5 μm conventional polypyrrole film before and after treatment with 0.2M NaOH and 1% HBF_4

- Untreated $1.0\ \mu\text{m}$ conventional polypyrrole film
- Equivalent microfibrillar film

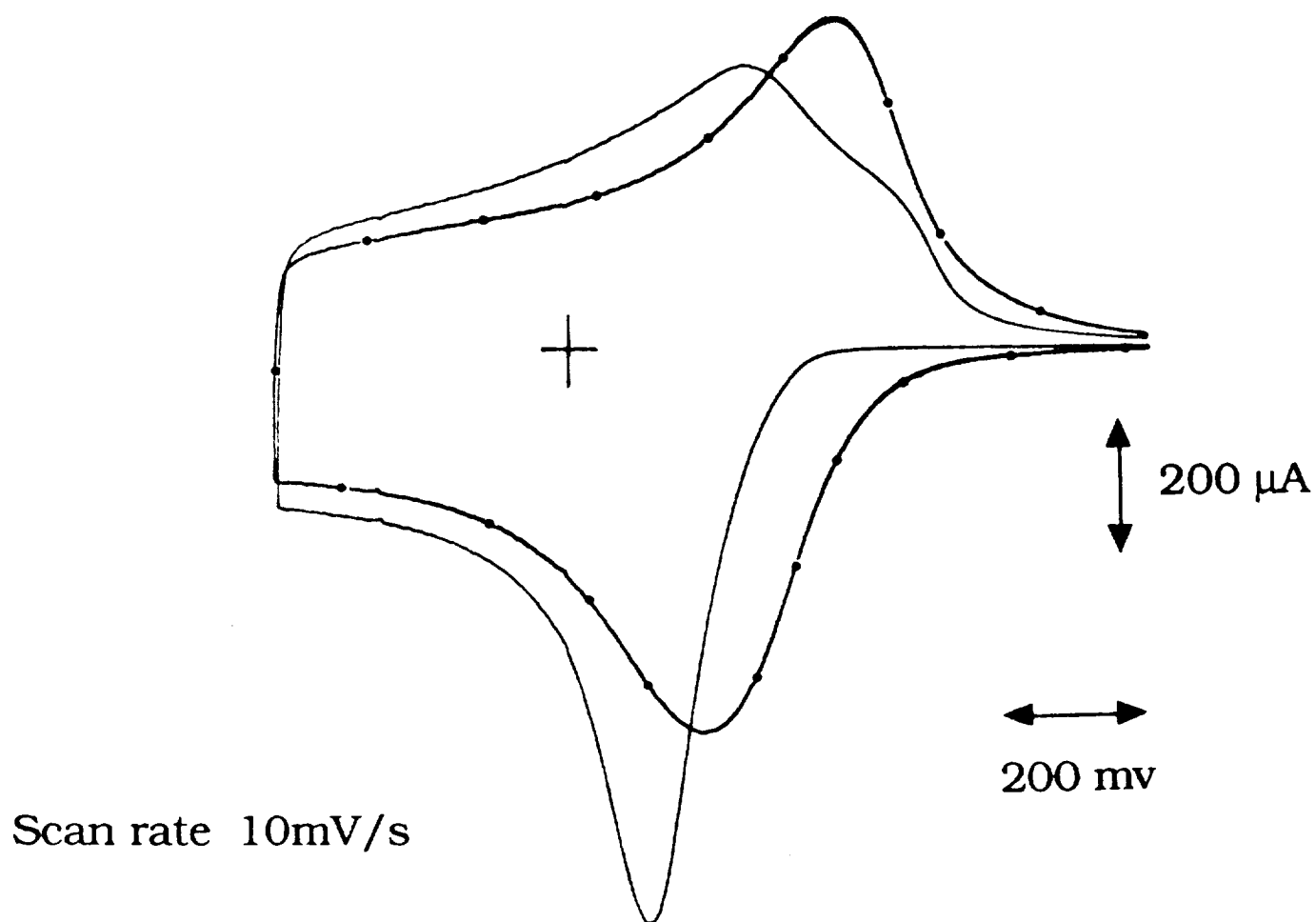


Fig. 3. Cyclic voltammogram of an untreated $1.0\ \mu\text{m}$ conventional polypyrrole film and a cyclic voltammogram of the equivalent microfibrillar film

- Treated 1.0 μm conventional polypyrrole film
— Equivalent microfibrillar film

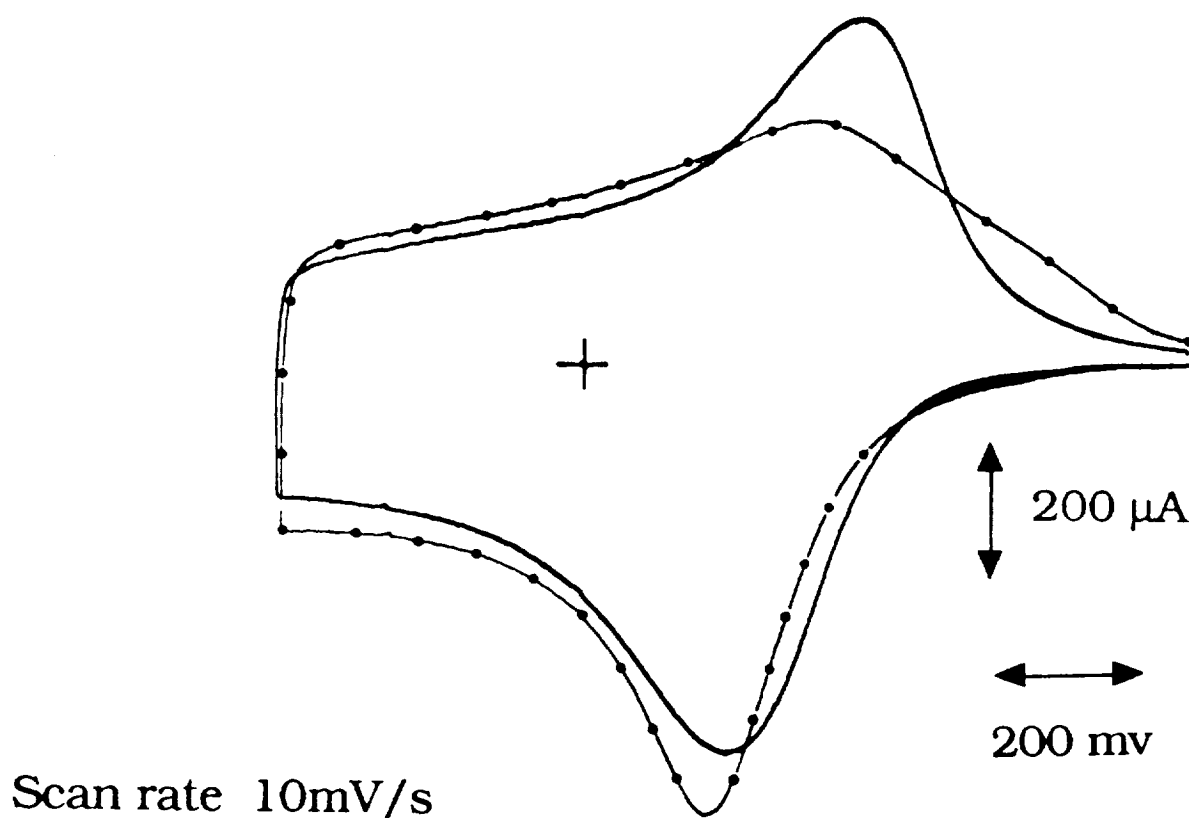


Fig. 4. Cyclic voltammogram of a treated 1.0 μm conventional polypyrrole film and a cyclic voltammogram of the equivalent microfibrillar film

1st/2nd oxidations - treated flat film

20Jul5 vs. 20Jul7

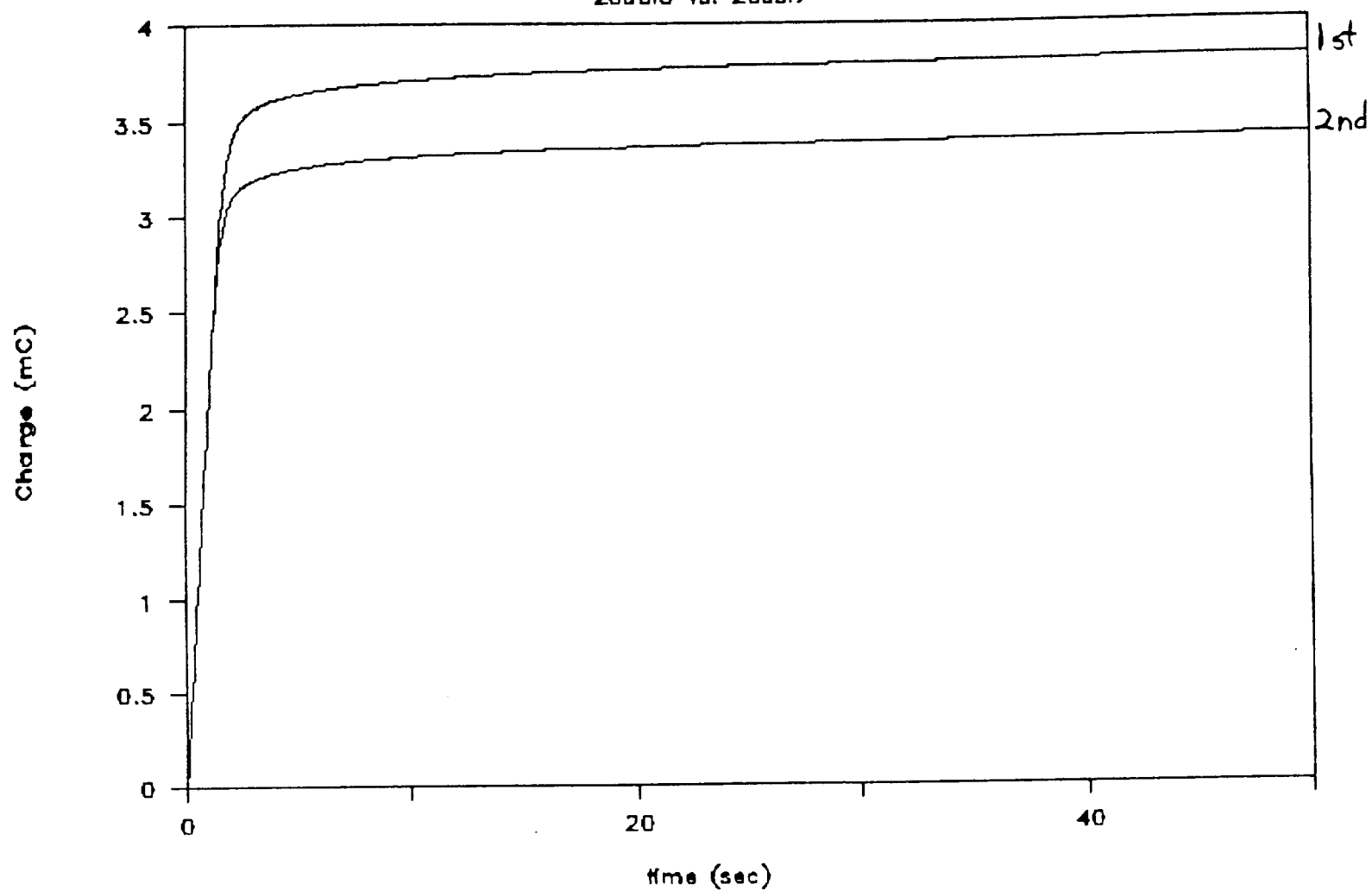


Fig. 5. Charge/time transients comparing 1st vs. 2nd oxidations of a treated flat polypyrrole film.

1st/2nd reductions - treated flat film

20Jul6 vs. 26Jul8

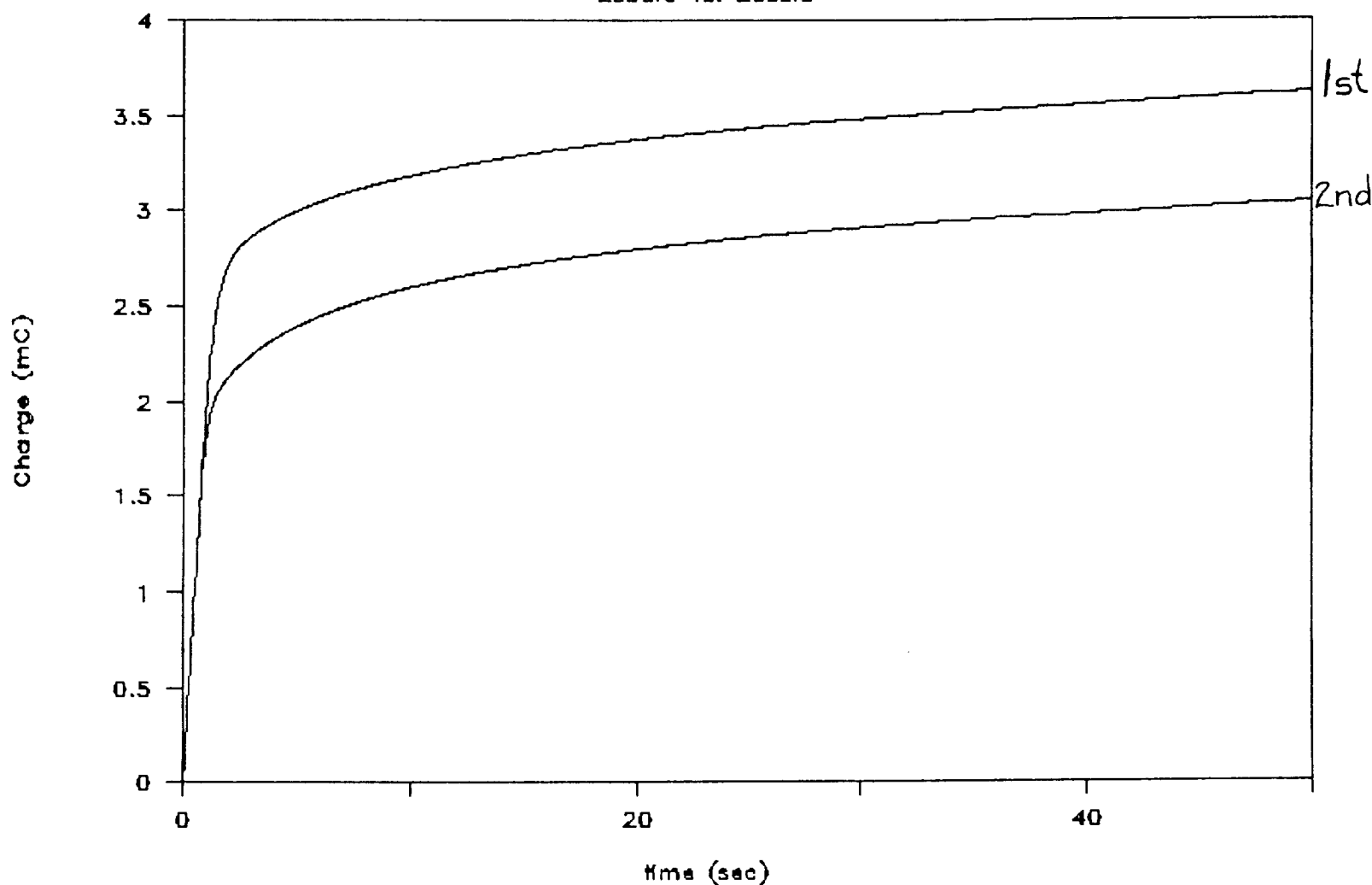


Fig. 6. Charge/time transients comparing 1st vs. 2nd reductions of a treated flat polypyrrole film.

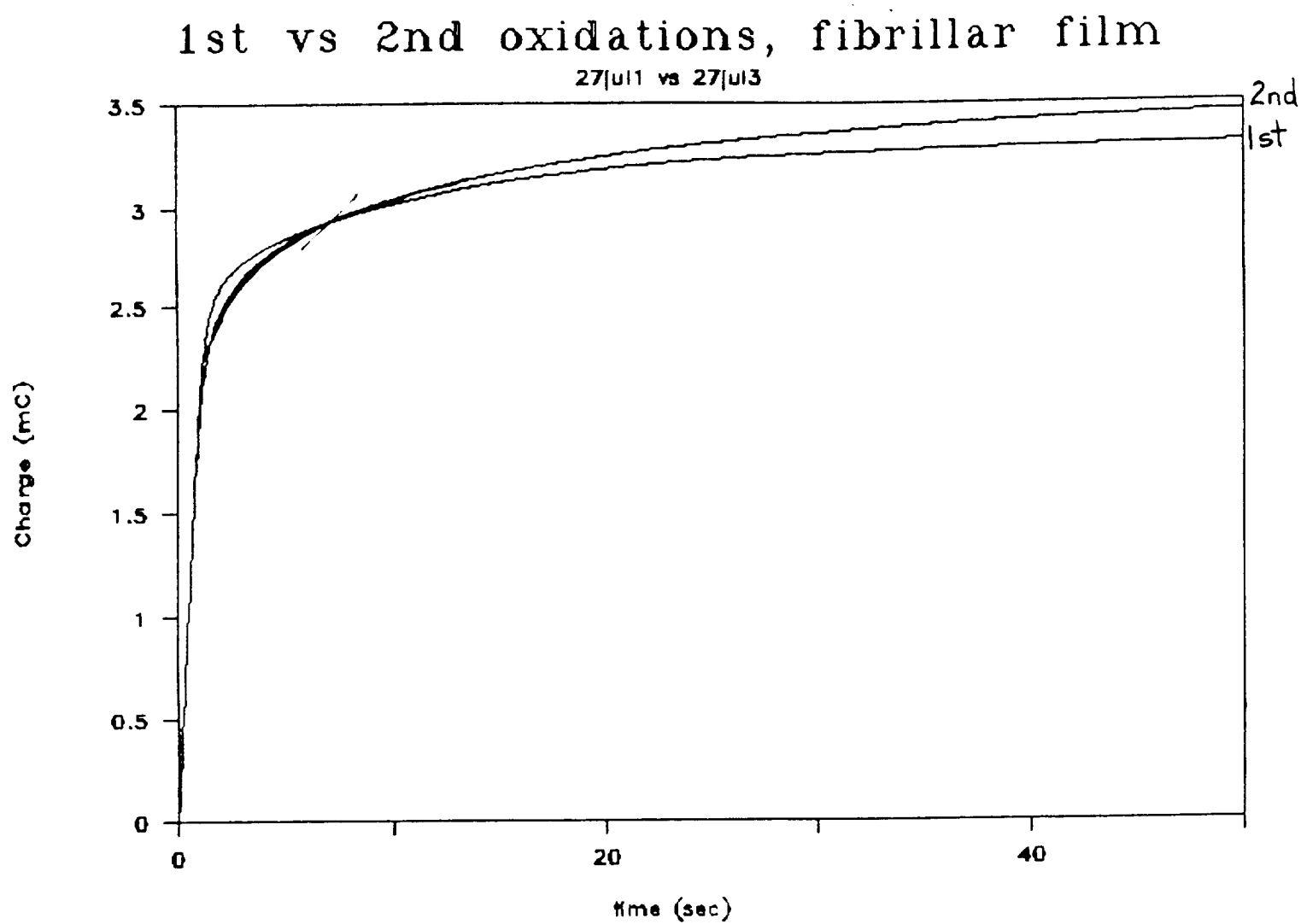


Fig. 7. Charge/time transients comparing 1st vs. 2nd oxidations of a fibrillar polypyrrole film.

1st vs 2nd reductions, fibrillar film

27/ul2 vs 27/ul4

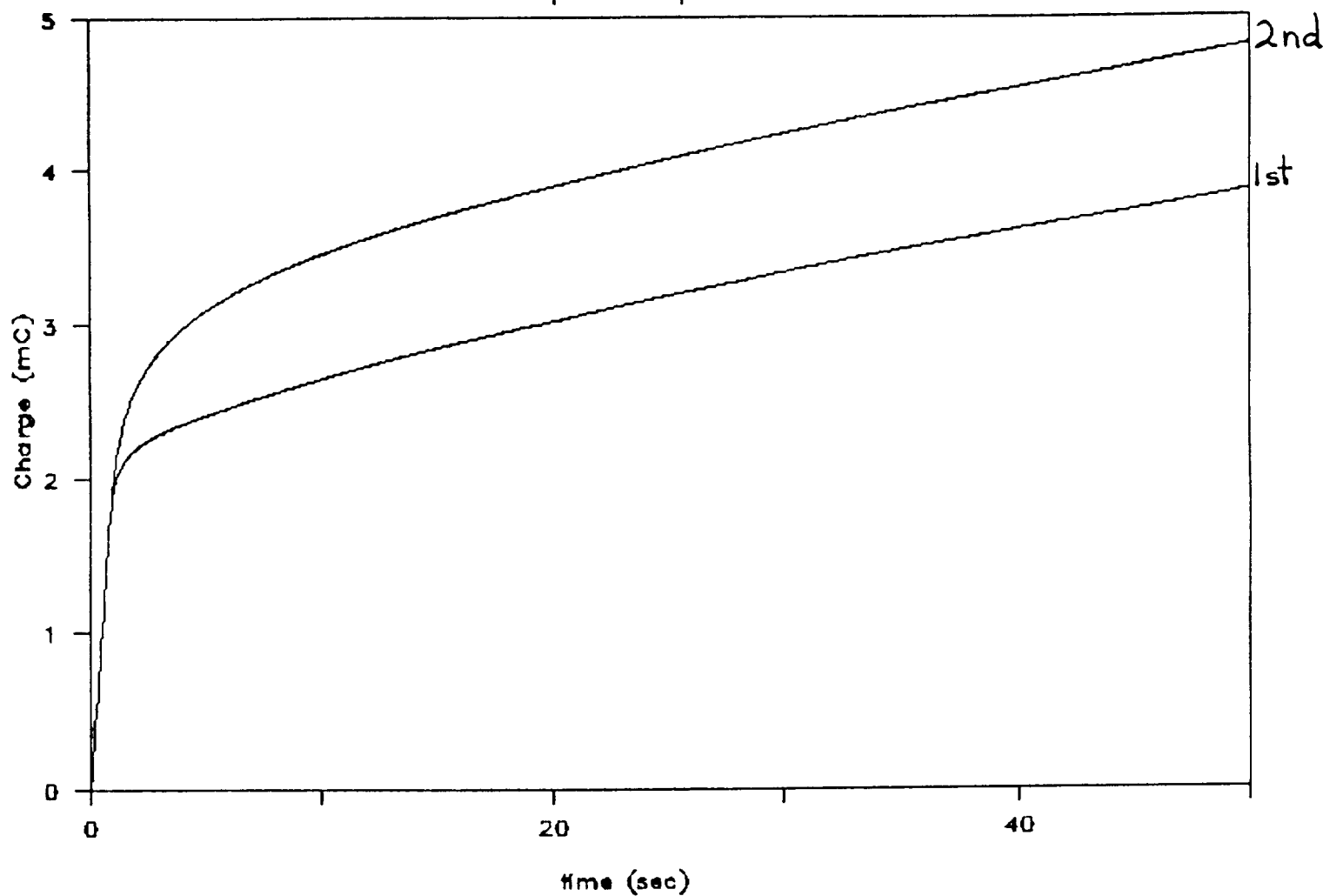
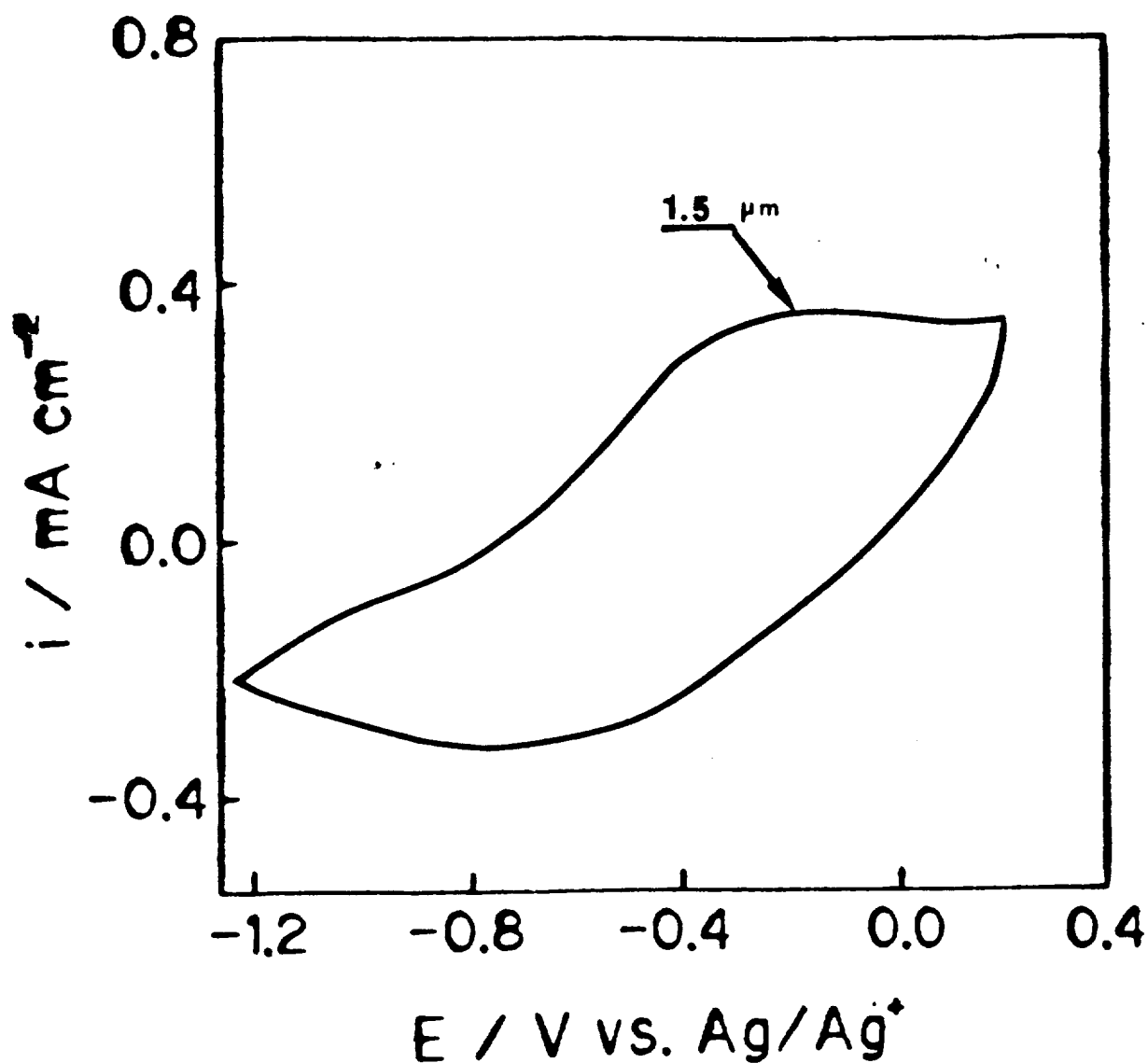


Fig. 8. Charge/time transients comparing 1st vs. 2nd reductions of a fibrillar polypyrrole film.



Cyclic voltammograms for polypyrrole electrodes formed at 0.32V with various thicknesses of the films at 5 mV s^{-1} . Film thickness of polypyrrole films is represented in terms of the film formation charges (C cm^{-2}) in the figure.

Fig. 9. Cyclic voltammogram of Osaka's Li/1M LiClO₄, PC/PPy battery system with 1.5 μm film.

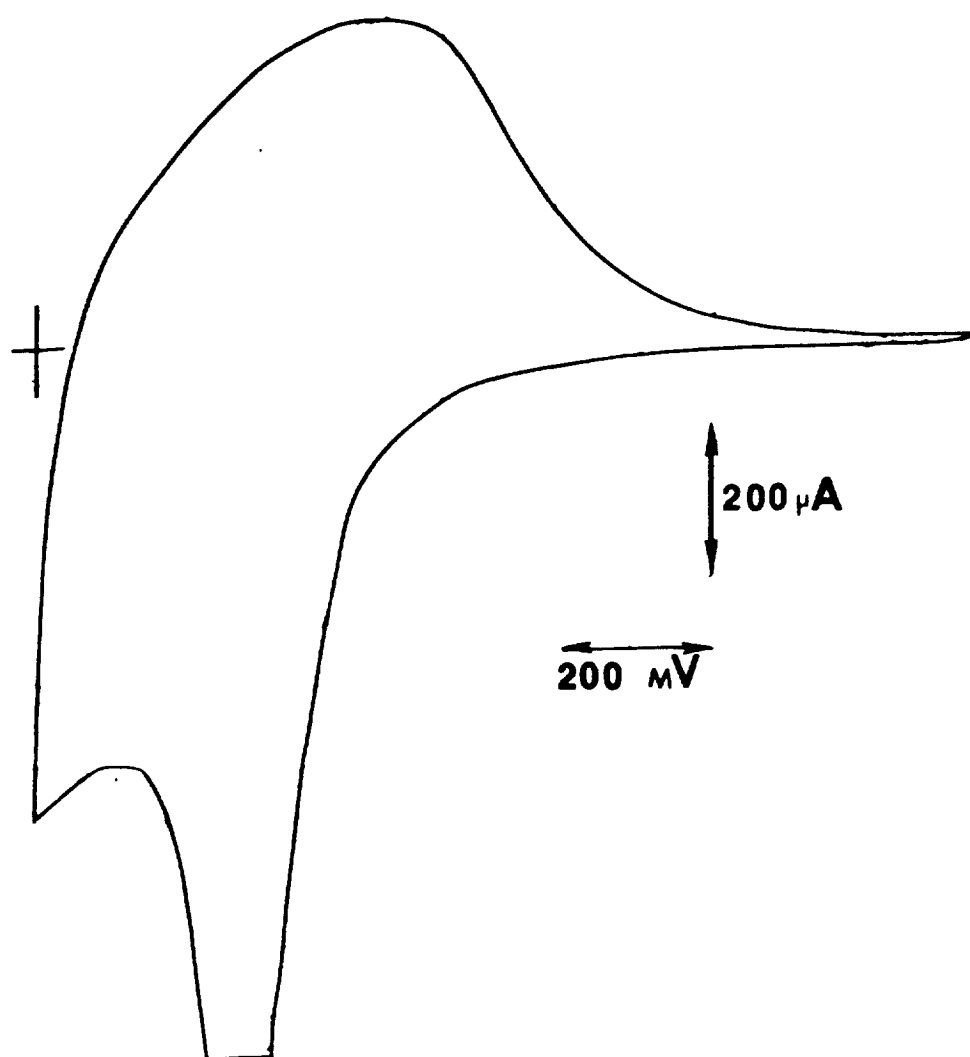


Fig. 10. Cyclic voltammogram of Martin's Li/1M LiClO₄, PC/PPy battery system with 1.5 μm film

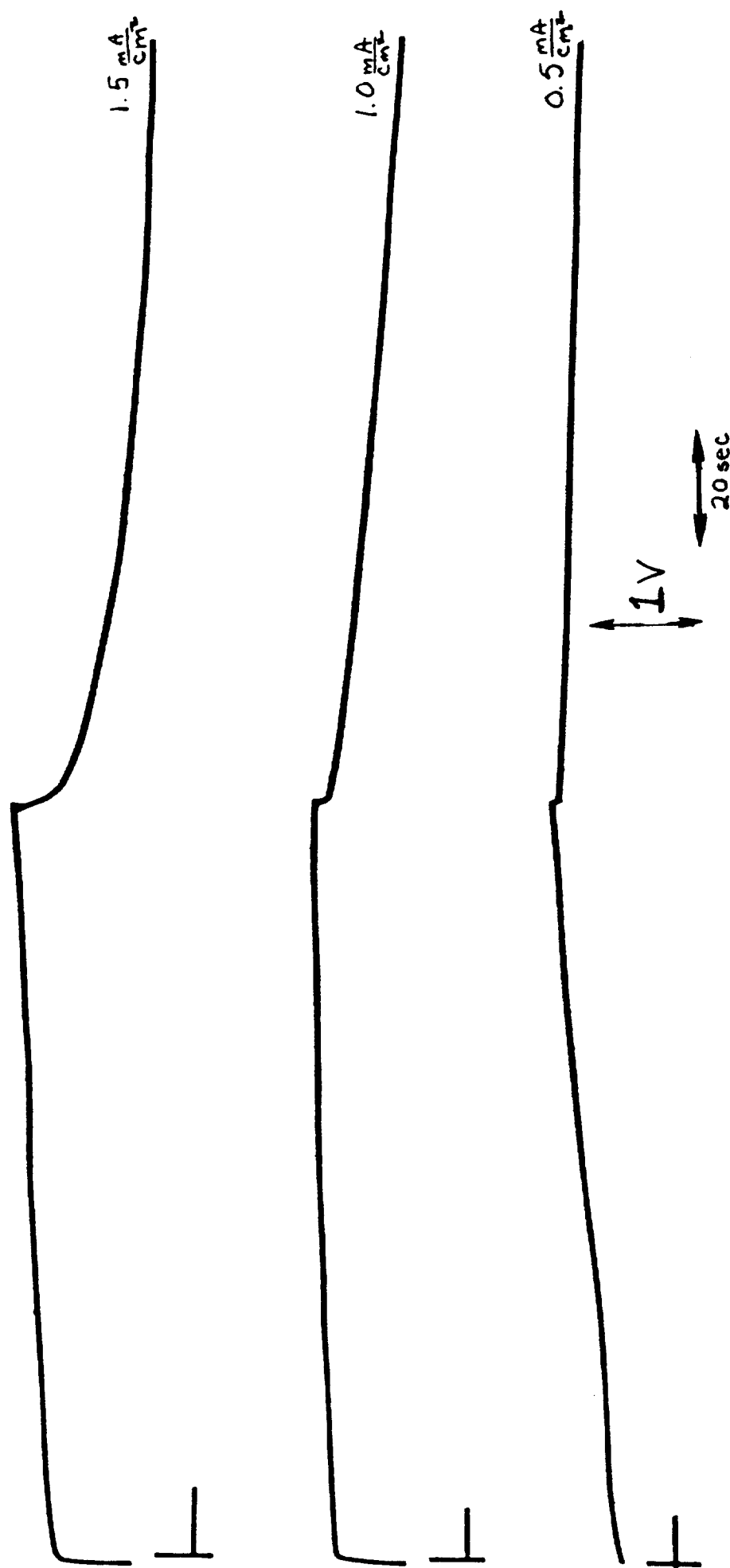


Fig. 11. Charge/Discharge curves of Li/PPy Battery with
1.5 μm flat film.

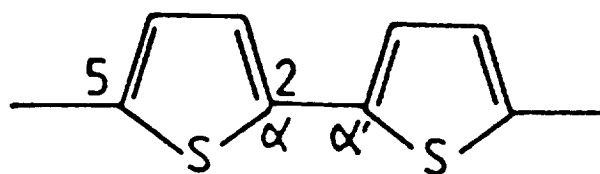


Fig. 12. General structure of polythiophene.

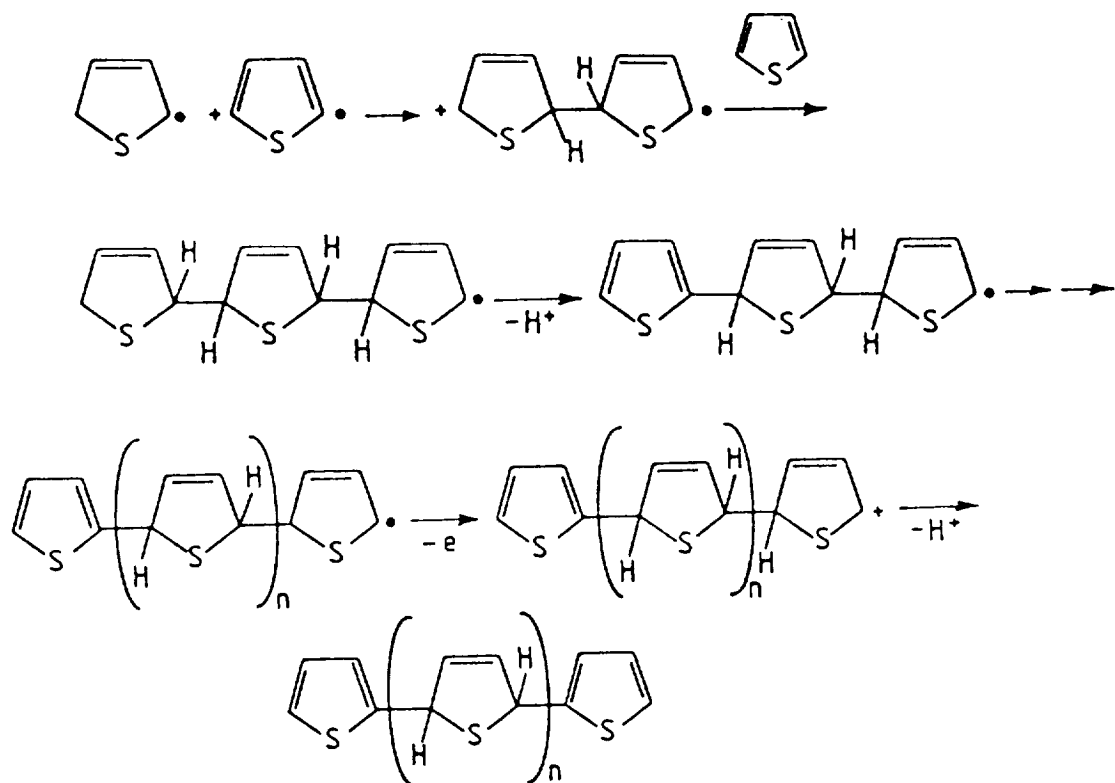


Fig. 13. Electrochemical polymerization mechanisms of polythiophene.

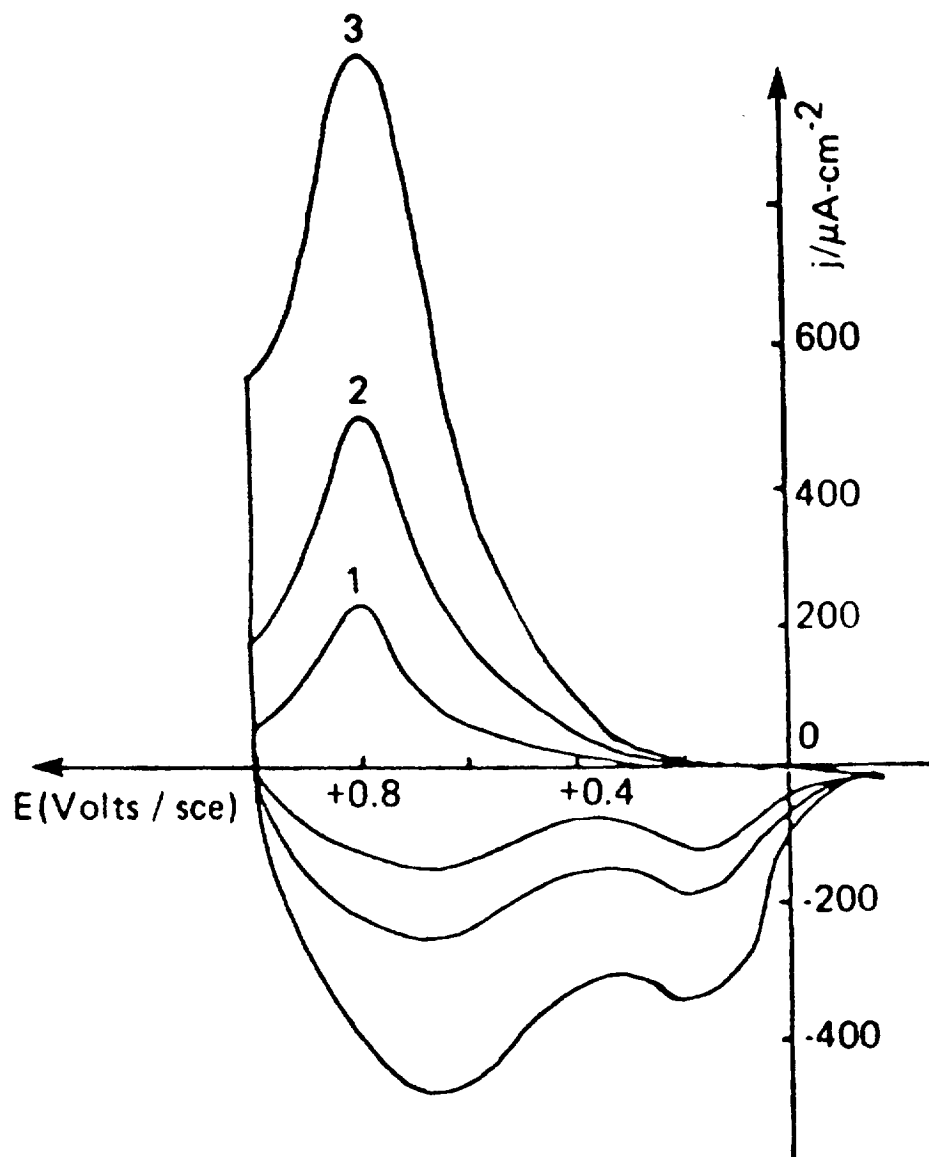


Fig. 14. Cyclic voltammograms of 250 nm poly-3-methylthiophene grafted on Pt with sweep rates of 20, 50, and 100 mV/s (electrolytic medium: $\text{CH}_3\text{CN} + 0.1\text{M LiClO}_4 + 0.01\text{M H}_2\text{O}$).